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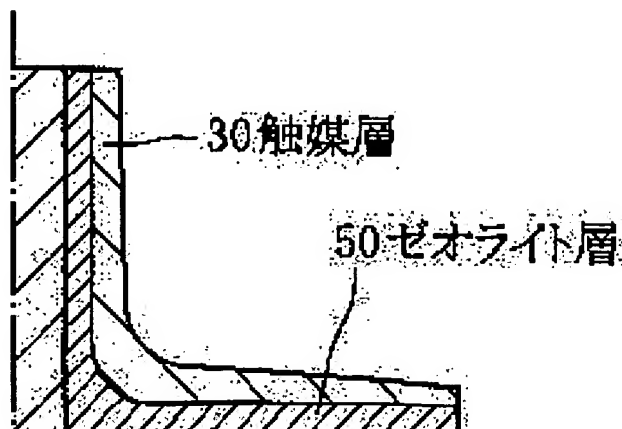
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country :**JP**(54) **CATALYST FOR PURIFYING EXHAUST GAS**

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent the deterioration of the durability and exhaust gas purifying capacity of a catalyst for purifying exhaust gas by restraining that an absorbent added to a catalyst layer penetrates into a catalyst support and the absorbent vaporizes and scatters from the catalyst.

SOLUTION: A zeolite, silica or titania layer 50 is formed between the catalyst layer 30 to which the absorbent is added and the catalyst support 10. The movement of the absorbent from the layer 30 to the support 10 is restrained by the layer 50 even when the catalyst is used over a long time at high temperature.



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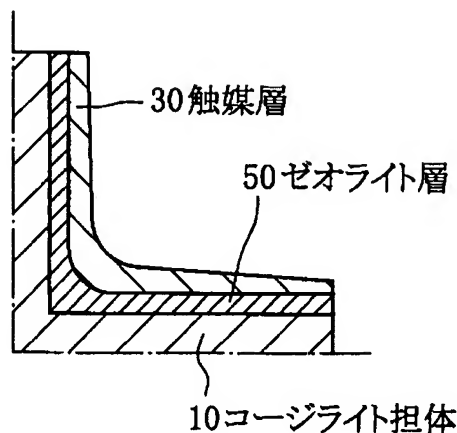
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(54) 【発明の名称】 排ガス浄化用触媒

(57) 【要約】

【課題】 排ガス浄化用触媒において、触媒層に添加された吸蔵剤の担体内への浸透や吸蔵剤の触媒からの蒸発、飛散を抑制し、触媒の耐久性および排ガス浄化能力の低下を防止する。

【解決手段】 吸蔵剤が添加された触媒層 (30) と担体 (10) との間にゼオライト層 (50) またはシリカ層またはチタニア層が形成される。触媒を長時間にわたって高温下で使用した場合にも、触媒層 (30) から担体 (10) への吸蔵剤の移動がゼオライト層 (50) またはシリカ層またはチタニア層により抑制される。



【特許請求の範囲】

【請求項1】 担体と触媒層とを含み、この触媒層にアルカリ金属及びアルカリ土類金属からなる群から選択される少なくとも一つを吸蔵剤として添加してなる排ガス浄化用触媒において、触媒中に抑制層を設けて上記触媒における上記吸蔵剤の移動を抑制することを特徴とする排ガス浄化用触媒。

【請求項2】 上記担体と上記触媒層との間および上記触媒層中或いは上記触媒層の外面の少なくとも一ヶ所に上記抑制層を形成したことを特徴とする請求項第1項に記載の排ガス浄化用触媒。

【請求項3】 上記抑制層が、IⅤ族、Ⅴ族及びⅥ族の遷移元素ならびにIⅤ族、Ⅴ族及びⅥ族の典型元素から選択される少なくとも一つの酸性物質を含む酸性酸化物と、上記少なくとも一つの酸性物質を含む複合酸化物と、窒素酸化物と上記吸蔵剤との反応性を阻害しない材料と、還元物質を吸着する材料とからなる群から選択される一つ以上の材料から構成されることを特徴とする請求項第1項または第2項に記載の排ガス浄化用触媒。

【請求項4】 上記抑制層がゼオライトからなることを特徴とする請求項第1項または第2項に記載の排ガス浄化用触媒。

【請求項5】 上記吸蔵剤はカリウムを含み、上記担体は多孔質担体からなることを特徴とする請求項第1項ないし第4項のいずれかに記載の排ガス浄化用触媒。

【請求項6】 上記抑制層は、酸性度の高い層、比表面積の高い層、結晶格子の小さい層、分子量の大きい元素化合物からなる層、或いは、塩基性度の高い層のいずれか一つで構成されることを特徴とする請求項第1項、第2項または第5項に記載の排ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、排ガス浄化用触媒に関し、特に、耐久性および排ガス浄化性能に優れた排ガス浄化用触媒に関する。

【0002】

【関連する背景技術】リーンバーンエンジンや筒内噴射式エンジン等の希薄燃焼式エンジンは、燃費特性や排ガス特性の向上のため、所定運転域では理論空燃比よりも燃料希薄側のリーン空燃比で運転される。リーン空燃比運転が行われる間は、排ガス中のNO_x（窒素酸化物）を三元触媒によって十分に浄化することができないことから、酸化雰囲気において排ガス中のNO_xを吸蔵するNO_x触媒を装備し、この触媒に吸蔵されたNO_xを還元雰囲気中でN₂（窒素）に還元させることにより、大気へのNO_x排出量を低減させることが知られている。この種の吸蔵型リーンNO_x触媒において、例えば特開平9-85093号公報に記載のように、カリウム（K）をNO_x吸蔵剤として添加してNO_x吸蔵性能を向上す

るようにしたものがある。

【0003】

【発明が解決しようとする課題】しかしながら、吸蔵剤たとえばカリウムを添加したNO_x触媒を長時間にわたって高温下におくと、触媒にクラックが発生することがあり、NO_x触媒の耐久性低下の原因になっている。NO_x触媒におけるクラック発生の原因を究明するべく、本発明者らは、ハニカム型のコージライト担体に担持した触媒層にカリウムを吸蔵剤として添加してなるNO_x触媒を製造し、このNO_x触媒を装備したエンジンの台上試験ならびにこの種のエンジンを搭載した車両の走行試験を行った。台上試験や実車走行試験では、NO_x触媒が相当な時間にわたって650℃以上という高温に曝されるような条件でエンジンや車両を運転した。そして、運転終了後にNO_x触媒の切断面における元素分析をEPMA法（電子線プローブ微小部分分析法）により実施し、触媒のコージライト（Mg₂Al₄Si₅O₁₈）層中にカリウム、マグネシウム、アルミニウム、珪素及び酸素の化合物KMg₄Al₉Si₃₆O₃₆やカリウム、アルミニウム、珪素及び酸素の化合物KAlSiO₄が存在することを確認した。

【0004】上記の実験によれば、NO_x触媒が高温に曝されると、触媒層（ウオッシュコート）に添加されたカリウムがコージライト担体内に浸透し、高温雰囲気下においてカリウムがコージライトと反応して上記の化合物を形成するものと考えられる。ここで、カリウムの化合物はその水溶性が高く且つその融点が高いことからコージライト担体へカリウムが浸透し易いと解される。そして、コージライトと熱膨張率を異にする化合物がコージライト担体中に形成されると、触媒使用中および使用前後における触媒温度の変化に伴ってコージライト担体にクラックが発生してNO_x触媒の強度が低下することになる。

【0005】上述のように、カリウム等を吸蔵剤として含むNO_x触媒は酸化雰囲気下で使用される。この酸化雰囲気では、吸蔵剤と排ガス中の窒素成分や硫黄成分との化学反応により吸蔵剤の硝酸塩や硫酸塩が形成され、NO_x吸蔵能力が低下する。この場合、NO_x触媒まわりに還元雰囲気を形成して硝酸塩や硫酸塩を分解することにより吸蔵能力を回復可能であるが、このような対策を講じて、NO_x触媒を高温下で長時間使用すると浄化性能が低下することがある。

【0006】本発明者が行った下記実験の結果からみて、浄化性能低下原因の一つは、高温下において吸蔵剤がNO_x触媒から徐々に蒸発、飛散して触媒内の吸蔵剤のかなりの部分が消失することにあると考えられる。即ち、本発明者は、カリウムを吸蔵剤として含む触媒層をコージライト担体に担持してなるNO_x触媒を製作し、未使用のNO_x触媒におけるカリウム含有率をXRF法（蛍光X線分光分析法）で求め、次に、この触媒を高温

下で長時間（例えば850℃で32時間）にわたって使用した後に触媒のカリウム含有率を求め、更に、使用前後におけるカリウム含有率の差を当初のカリウム含有率で除してカリウム消失量を求めた。この結果、カリウム消失量は数十%ないし50%に及ぶことが分かった（図6を参照）。

【0007】そこで、本発明は、吸蔵剤の消失による排ガス浄化性能の悪化度合いを大幅に低減可能な排ガス浄化用触媒を提供することを目的とする。

【0008】

【課題を解決するための手段】本発明は、触媒層に吸蔵剤を添加してなる排ガス浄化用触媒に、吸蔵剤の移動を抑制する材料からなる抑制層を設けて、触媒における吸蔵剤の移動を抑制することを特徴とする。本発明において、排ガス浄化用触媒が高温に晒された場合に触媒内を移動する吸蔵剤は、抑制層により移動が抑制される。抑制層は層状をなすものであり、このような抑制層の形成形態は吸蔵剤の移動の抑制に大きく寄与し、触媒からの吸蔵剤の蒸発、飛散による吸蔵剤の消失ひいては触媒の排ガス浄化性能の低下が防止される。

【0009】本発明において、好ましくは、抑制層は酸点を有する材料により構成される。この場合、触媒内を移動する吸蔵剤は、抑制層の構成材料が有する酸点において捕捉されて固定されるものと解され、触媒における吸蔵剤の移動を効果的に抑制できる。本発明において、好ましくは、抑制層は、担体と触媒層との間および触媒層の外面の少なくとも一方に形成される。

【0010】担体と触媒層との間に設けた場合、例えば担体を抑制層で被覆した場合、触媒層に添加された吸蔵剤の担体内への浸入が、触媒層と担体との間に層状をなして設けられた抑制層によって確実に阻止される。そして、抑制層により担体内への吸蔵剤の浸入が抑制されるので、吸蔵剤を構成する材料の組成成分と担体の組成成分との反応による化合物の形成が抑制され、この化合物の形成に起因する担体でのクラック発生ひいては触媒の耐久性低下が防止される。また、抑制層を触媒層の外面に形成した場合、触媒層からの吸蔵剤の蒸発、飛散が、触媒層の外面に層状をなして設けた抑制層によって確実に阻止される。なお、本発明の触媒は複数の触媒層を備えたものでも良く、この場合、触媒層の配置に応じて一つまたは2つ以上の抑制層が触媒中の適宜の位置に配される。

【0011】一般に、多数のセルからなる担体に触媒層を担持してなる触媒では、担体表面からの触媒層の剥離防止等の、触媒に課せられる機械的、物理的または化学的な要件を満たすため、担体の各セルのコーナー部では触媒層の層厚を厚くしており、従って、コーナー部付近で触媒層は深層部を有することになる。既に述べたように、触媒層内の吸蔵剤と燃料中の硫黄成分との反応により生成される硫酸塩を分解して吸蔵性能を回復させるべ

く排気空燃比をリッチ化するなどして還元雰囲気を形成するが、触媒層の深層部ではガス拡散が悪いので硫酸塩の分解は困難であり、硫酸塩の粒子成長が進行し易く、これに伴う吸蔵剤の消費によってNOx吸蔵性能が低下する。

【0012】この点、担体と触媒層との間や触媒層の外面に抑制層を形成してなる本発明の好適態様では、担体コーナー部の触媒層を厚くすべきとの要件が緩和され、触媒層の層厚が全体として均一にできて触媒層でのガス拡散が促進され、硫酸塩の成長に伴う吸蔵剤の消費量が少なくなる。本発明において、好ましくは、抑制層は、酸性物質を含む複合酸化物からなる群から選択される少なくとも一つの材料から構成される。酸性物質を含む複合酸化物の各々は、IV族、V族およびVI族の遷移元素ならびにIV族、V族およびVI族の典型元素からなる群から選択される少なくとも一つの酸性物質を含む。

【0013】この好適態様では、吸蔵剤固定能力および熱安定性に富む酸性酸化物や複合酸化物により、触媒の排ガス浄化性能低下の防止および耐久性向上が図られる。たとえば、複合酸化物は酸点が発現する組合せの酸化物から構成される。より好ましくは、少なくとも一つの酸性物質は、酸性物質と吸蔵剤との反応性を考慮して選択される。例えば、吸蔵剤がカリウムの場合、シリカやタングステンを酸性物質として含む酸性酸化物や複合酸化物を用いるのが良い。

【0014】好ましくは、抑制層は、NOxと吸蔵剤との反応性を阻害しない材料からなる。この場合、触媒上での吸蔵剤の移動を抑制する作用が抑制層により奏されると共に、吸蔵剤のNOx吸蔵作用が良好に奏される。或いは、抑制層は、還元物質（たとえば、HCなどの還元ガス）を吸着する材料からなる。この場合、抑制層の還元物質吸着能により抑制層中に捕捉された還元物質により、触媒層内や抑制層内の硫酸塩や硝酸塩が分解され、NOx吸蔵性能が回復する。

【0015】好ましくは、抑制層はゼオライトからなる。ゼオライトを抑制層として備えた触媒によれば、既に述べた好適態様の利点と同様の利点が奏される。すなわち、ゼオライトはカチオン交換能と分子ふるい作用を有し、吸蔵剤を固定する能力およびHCを吸着する能力に優れる。触媒内を移動する吸蔵剤は、高温の水蒸気存在下においてイオン化された状態になることがあり、ゼオライト上の酸点のカチオン交換能によりイオンとして固定される（図5を参照）。また、ゼオライトは、三次元網目状構造をもち、高い比表面積を有する。吸蔵剤は、このような構造のゼオライト上で高分散化するので、特にゼオライトを触媒層と担体との間に設けた場合、吸蔵剤は担体内へ浸入し難くなる。更に、ゼオライトはHC吸着能（より一般的には還元物質吸着能）に優れる。内燃機関がリーン運転状態であっても排ガスには僅かなHCが含まれ、ゼオライト上に吸着されたHCによって

吸蔵剤の硝酸塩や硫酸塩の分解が促進される。すなわち、リーン運転中においても、HC吸着能を有するゼオライトからなる抑制層は、排ガス中に含まれる僅かなHCを利用して吸蔵剤の硝酸塩や硫酸塩を連続的に分解し、触媒のNO_x吸蔵性能の回復に寄与する。

【0016】本発明において、抑制層を構成するゼオライトとして、MF I型、Y型、X型、モルデナイト、フェリエライトなどの種々のタイプのゼオライトを使用可能であるが、吸着HC種との構造関連性を考慮して、排ガス組成に適合するものを選択することが好ましい。また、ゼオライトのカチオン交換能及び耐熱性能は、ゼオライトの組成成分に依存する。すなわち、カチオン交換能はゼオライトでのSiO₂/AlO₂比に反比例し、耐熱性はこの比に比例する。従って、例えば、上記の比をできるだけ大きくすることにより触媒の耐熱性向上を図ることができる。また、上記の比を小さくすることにより触媒の高温下での長時間運転に伴う吸蔵剤の消失量を低減して吸蔵性能を維持できる。

【0017】好ましくは、抑制層は、触媒物質たとえば貴金属を含まない。この場合、抑制層内では触媒物質による触媒作用は奏されず、抑制層に固定された吸蔵剤と排ガス中のSO_xとの化学反応が生じ難くなるため、この化学反応に伴う吸蔵剤の消費が少なくなり、触媒のNO_x吸蔵性能が維持される。本発明において、好ましくは、吸蔵剤はカリウムを含み、担体は多孔質担体からなる。カリウムの添加により触媒のNO_x吸蔵能力が向上する。また、多孔質担体の使用により排ガスの圧力損失が低下すると共に排ガスが触媒層に良好に接触して排ガス浄化が良好に行われる。その一方で、多孔質担体を有する触媒では、高温の水蒸気を含む排ガスの流通が良くなって吸蔵剤の移動や蒸発、飛散が生じ易くなるが、本発明では抑制層によってこれが防止される。

【0018】好ましくは、上記抑制層は、酸性度の高い層、比表面積の高い層、結晶格子の小さい層、分子量の大きい元素化合物からなる層、或いは、塩基性度の高い層のいずれか一つで構成される。好ましくは、酸性度の高い層は、触媒層のカリウムとの反応性が高い酸性材料たとえば珪素酸化物を含む。比表面積の高い層は、比表面積の高い材料たとえばゼオライトを含む。分子量の大きい元素化合物からなる層は、例えば分子量が大きく且つ安定な塩基材料たとえば硫酸バリウム(BaSO₄)から構成される。また、塩基性度の高い層は、たとえば酸化バリウム(BaO)などの塩基材料からなる。

【0019】上記の好適態様によれば、多孔質担体へのカリウムの浸透が、下記のメカニズムによって抑制されるものと考えられる。すなわち、抑制層が酸性度の高い層から構成されている場合、カリウムは酸性度の高い層と反応して多孔質担体の表面に到達する前に消費されるものと解される。また、比表面積の高い層からなる抑制層の内部ではカリウムが高分散し、結晶格子の小さい層

からなる抑制層はカリウムの移動を阻止するものと解される。分子量の大きい元素化合物からなる抑制層の場合、多孔質担体へのカリウムの浸透経路が少なくなるものと考えられる。そして、塩基性度の高い抑制層の場合には、この層がカリウムと同一の性質を有することから、カリウムが抑制層に近づくとき反発を受け、多孔質担体へのカリウムの誘導性が低下するものと解される。

【0020】上記のようにして多孔質担体へのカリウムの浸透が抑制されて排ガス浄化触媒の耐久性向上が図られる。また、カリウムを消費せずにその浸透を抑制可能な抑制層の場合、カリウムの消費によるカリウムのNO_x浄化作用の低下を来すことがなく、排ガス浄化用触媒の排ガス浄化性能が好適に維持される。本発明の排ガス浄化用触媒の耐久性および吸蔵剤消失防止能力を評価するため、その一例としてカリウムを含む吸蔵剤を添加した触媒層とコージライト担体との間にゼオライトを抑制層として設けてなるNO_x触媒を製作し、未使用のNO_x触媒におけるカリウム含有率をXRF法で求めた。また、NO_x触媒をエンジンに搭載して台上試験や実車走行試験に供し、これにより高温下で長時間(例えば850°Cで32時間)にわたって使用したNO_x触媒のカリウム含有率を求め、使用前後におけるカリウム含有率の差を当初のカリウム含有率で除したものをカリウム消失量として求めた。この結果、触媒層を担体に担持した触媒では数十%ないし50%に及ぶカリウム消失量が、本発明の触媒では十数%程度に抑制されることが分かった。この実験結果(図6)は、吸蔵剤であるカリウムの触媒からの消失量が本発明により大幅に低減されることを示す。

【0021】また、本発明による上記NO_x触媒を台上試験や実車走行試験に供した後でその切断面に関してEPMA法により元素分析した。この結果、コージライト担体内でのカリウム、マグネシウム、アルミニウム、珪素及び酸素の化合物やカリウム、アルミニウム、珪素及び酸素の化合物の存在量は、コージライト担体の表面に単に触媒層を形成してなる触媒の場合に比べ相当に少ないことが認められた。

【0022】この実験結果は、コージライト担体(より一般的には多孔質担体)中へのカリウムの浸透が抑制層により防止されることを示す。実際、本発明の排ガス浄化用触媒は、高温下で長時間使用した場合にも、カリウムの浸透に起因した化合物の生成が防止されて多孔質担体にクラックが発生しにくく、耐久性に富む。

【0023】

【発明の実施の形態】以下、本発明の第1実施形態による排気ガス浄化触媒を説明する。本実施形態の排気ガス浄化触媒は、多数のセルからなるハニカム(モノリス)型のコージライト担体を有するNO_x触媒として構成されている。図1はコージライト担体の一つのセルの一部を示し、コージライト担体10のセルは例えば四角形状

に形成されている。コージライト担体10の表面にはシリカ層20が被覆され、また、シリカ層20の表面に触媒層30が担持されている。そして、触媒層30には、カリウム(K)およびバリウム(Ba)がNO_x吸蔵剤として添加されている。シリカ層20は、コージライト担体10(より一般的には多孔質担体)へのカリウムの浸透を抑制する抑制層として機能する。

【0024】コージライト担体10は、たとえば、アルミナ源の粉末、シリカ源の粉末およびマグネシア源の粉末を、アルミナ、シリカ、マグネシアの割合がコージライト組成になるように混合したものを水に分散させ、その固形分をハニカム状に成形し、このハニカム成形体を焼成したものである。シリカ層20は、例えば以下のようにして、コージライト担体10の表面に形成される。まず、珪素化合物の水溶性塩を水で希釈して所定濃度の水溶液を調製し、この水溶液中にコージライト担体10を浸漬する。珪素化合物の塩の水溶液は、コージライト担体10の吸水性によってコージライト担体10の表面や表層中に吸収される。その後、コージライト担体10を乾燥させて水分を蒸発させ、珪素化合物の塩をコージライト担体10の表面や表層中に吸着させる。次に、コージライト担体10を加熱すると、珪素化合物の塩が分解し、コージライト担体10の表面にシリカ層20が形成される。すなわち、コージライト担体10がシリカ層20により被覆される。

【0025】シリカ層20の形成に用いられる珪素化合物の塩の水溶液の適正な濃度は、主としてコージライト担体10の吸水特性に応じて変化する。そこで、コージライト担体の表層部分についてEPMA法などによる元素分析を行って、水溶液濃度と被覆状態との関係を予め確認しておくことが好ましい。この様に珪素化合物の塩の水溶液の最適濃度を予め求めることにより、コージライト担体と触媒層との接着性ならびにシリカ層のカリウム浸透抑制効果を担保する最適な被覆状態を得ることができる。

【0026】触媒層30は、例えば以下のようにして、シリカ層20の表面に形成される。まず、プラチナなどの貴金属とカリウムなどのアルカリ金属とバリウムなどのアルカリ土類金属とを主成分とする粉末を含むスラリーが調製される。次いで、シリカ層20を形成済みのコージライト担体10を上記のスラリー中に浸漬し、これを乾燥後に焼成する。

【0027】以上のようにして、シリカ層20を介してコージライト担体10に触媒層30をコーティングしてなるNO_x触媒を得る。従来公知のように、このNO_x触媒は、たとえば緩衝材を介してケースに収容され、希薄燃焼内燃機関の排気管内に配置される。このNO_x触媒によれば、リーン空燃比での機関運転中に排ガス中のNO_xが、触媒層30に分散された触媒種の作用下で硝酸塩の形で吸蔵される。また、リッチ空燃比での機関運

転中には硝酸塩が分解され、吸蔵されていたNO_xが窒素に還元されてNO_x触媒から大気中に放出される。

【0028】このようなNO_x触媒を装備した内燃機関を長時間運転すると、NO_x触媒は長時間にわたって高温に晒される。この場合、カリウムが添加された触媒層をコージライト担体にコーティングしてなる従来のNO_x触媒にあっては、既に述べたようにカリウムがコージライト担体中へ移動して担体中の珪素などと反応して化合物を生成し、コージライト担体にクラックが発生してNO_x触媒の耐久性を損なうことになる。これに対して、本実施形態のNO_x触媒では、EPMA法による元素分析によれば、NO_x触媒を長時間にわたって高温下で使用した場合にも、触媒層30に添加されたカリウムとコージライト担体10のシリカ成分との化合物の生成が抑制されることが明らかになった。この理由は、触媒層30からコージライト担体10へのカリウムの移動がシリカ層20により阻止されるものと考えられる。この様にコージライト担体10と熱膨張率を異にする化合物がコージライト担体10中で生成しないことから、化合物の生成に起因するコージライト担体10でのクラック発生が防止される。

【0029】以下、本発明の第2実施形態による排気ガス浄化触媒を説明する。図3に示すように、本実施形態の排気ガス浄化触媒は、第1実施形態のものに比べて、シリカ層20に代えて、二酸化チタン(TiO₂)を主成分とするチタニア層40を抑制層として形成した点が異なる。その他の点については第1実施形態のものと同一構成であり、この排気ガス浄化触媒は第1実施形態のものと略同様の方法で製造できる。

【0030】チタニア層40をコージライト担体10と触媒層30との間に形成してなる本実施形態の排気ガス浄化触媒においても、EPMA法による元素分析によれば、長時間にわたる高温下での使用した場合にも触媒層30に添加されたカリウムのコージライト担体10中への浸透が防止されることが分かった。この様に、カリウムの浸透が防止されるため、この排気ガス浄化触媒は耐久性に富む。また、本実施形態によるNO_x触媒では、触媒層30からのカリウムの損失が低減される。この理由もシリカ層と同様と考えられる。

【0031】以下、本発明の第3実施形態による排気ガス浄化触媒を説明する。図4に示すように、本実施形態の排気ガス浄化触媒は、第1実施形態のものに比べて、シリカ層20に代えて、ゼオライト層50を抑制層として形成した点が異なる。その他の点については第1実施形態のものと同一構成であり、この排気ガス浄化触媒は第1実施形態のものと略同様の方法で製造できる。

【0032】なお、コージライト担体10へのゼオライト層50の形成にあたり、第1実施形態の場合と同様にゼオライト構成成分を水系分散剤に分散させても良いが、有機性分散剤に分散させるようにしても良い。ま

た、接着剤としてシリカ、アルミナ等の水和物の水分分散品（ゾル）や帯電分散溶液（コロイド）を用いることもできる。

【0033】ゼオライト層50を抑制層として備えた本実施形態の触媒において、ゼオライト層50はカチオン交換能を備える酸点を有し、吸蔵剤（本実施形態ではカリウム）を固定する能力に優れる。触媒内を移動する吸蔵剤は、高温の水蒸気存在下においてイオン化された状態になることがあり、図5に模式的に示すように、吸蔵剤たとえばカリウムは、ゼオライト層50上の酸点のカチオン交換能によりイオンとして固定される。また、ゼオライト層50は、三次元網目状構造をもち、高い比表面積を有する。カリウムは、この様な構造のゼオライト上で高分散されるので、コージライト担体10内へ浸入し難くなる。更に、ゼオライト層50は、還元物質（たとえばHC等の還元ガス）を吸着する能力に優れる。内燃機関がリーン運転状態にあっても排ガスには僅かなHCが含まれ、HC吸着能を有するゼオライト層50上に吸着されたHCによってカリウムの硝酸塩や硫酸塩の分解が促進される。すなわち、リーン運転中においても、ゼオライト層50は、排ガス中に含まれる僅かなHCを利用して硝酸塩や硫酸塩を連続的に分解して、触媒のNOx吸蔵性能の回復に寄与する。

【0034】本実施形態のゼオライト層50は、触媒物質たとえばPt等の貴金属を含まず、従って、ゼオライト層50内ではPtなどによる触媒作用は奏されず、ゼオライト層50に固定されたカリウムと排ガス中のSOxの化学反応が生じ難くなるため、この様な化学反応に伴う吸蔵剤の消費が少なくなり、触媒のNOx吸蔵性能が維持される。

【0035】ゼオライト層50は、MFI型、Y型、X型、モルデナイト、フェリエライトなどの種々のタイプのゼオライトを用いて構成可能である。この際、吸着HC種との構造関連性を考慮して、排ガス組成に適合するタイプのゼオライトが選択される。また、ゼオライトのカチオン交換能は、ゼオライトでのSiO₂/AlO₂比に反比例し、その耐熱性はこの比に比例する。本実施形態では、耐熱性向上のため、上記の比をできるだけ大きくなるようにしている。なお、SiO₂/AlO₂比が小さくなるようにゼオライト組成成分を調製することにより、ゼオライトの吸蔵剤捕捉能力を増大可能であり、この場合、高温下の長時間使用による吸蔵剤の消失量が低減する。

【0036】ゼオライト層50をコージライト担体10と触媒層30との間に形成してなる本実施形態の排気ガス浄化触媒の耐久性および吸蔵剤消失防止能力を評価するため、カリウムを含む吸蔵剤を添加した触媒層とコージライト担体との間にゼオライトを抑制層として設けてなるNOx触媒を製作し、未使用のNOx触媒におけるカリウム含有率をXRF法で求めた。また、NOx触媒

をエンジンに搭載して台上試験や実車走行試験に供し、これにより高温下で長時間（例えば850°Cで32時間）にわたって使用したNOx触媒のカリウム含有率を求め、使用前後におけるカリウム含有率の差を当初のカリウム含有率で除したものをカリウム消失量として求めた。

【0037】図6に、ゼオライト層50を設けた本実施形態の触媒についての実験結果を、触媒層を担体に持持した未対策の触媒、シリカ層20を設けた第1実施形態の触媒及びチタニア層40を設けた第2実施形態の触媒についての実験結果と共に示す。図6に示すように、未対策の触媒でのカリウム消失量が数十%ないし50%に及ぶのに対して、本実施形態の触媒ではこのカリウム消失量が十数%程度に抑制されることが分かった。この実験結果は、吸蔵剤であるカリウムの触媒からの消失量が大幅に低減されることを示す。第1及び第2実施形態の触媒でのカリウム消失量は20数%程度であった。

【0038】また、第1及び第2実施例の場合と同様、本実施形態の触媒を台上試験や実車走行試験に供した後でその切断面に関してEPMA法により元素分析した。この結果、長時間にわたる高温下での使用した場合にも触媒層30に添加されたカリウムのコージライト担体10中への浸透が防止されることが分かった。本発明は、上記実施形態のものに限定されず、種々に変形可能である。

【0039】例えば、上記実施形態では、ハニカム型コージライト担体10を担体として用いたが、本発明は、コージライト以外の材料から成る担体を備えた排ガス浄化用触媒にも適用可能である。メタル担体を用いた場合には、担体への吸蔵剤の浸透はほとんど問題にはならないが、吸蔵剤の飛散を防止する効果が得られ、触媒の排ガス浄化性能の低下が防止される。また、ハニカム型コージライト担体を用いる場合、コージライト担体のセルは四角形状のものに限定されず、例えば三角形や六角形状のものでも良い。

【0040】第1実施形態では二酸化珪素を主成分とするシリカ層20によって抑制層を構成し、第2実施形態では二酸化チタンを主成分とするチタニア層40によって抑制層を構成し、また、第3実施形態ではゼオライト層50によって抑制層を構成したが、抑制層の構成材料は二酸化珪素や二酸化チタンやゼオライトに限定されない。

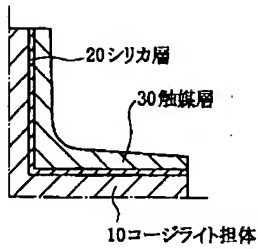
【0041】すなわち、二酸化珪素に代えて、他の酸性材料を用いて、抑制層を酸性度の高い層によって構成可能である。また、二酸化チタンに代えて、バリウム（Ba）などのアルカリ金属や酸化バリウム（BaO）などの塩基材料を主成分とする塩基性度の高い層によって抑制層を構成可能である。更に、ゼオライトなどの比表面積の高い材料を主成分として含む比表面積の高い層や、分子量が大きい安定塩基材料たとえば硫酸バリウムを主

成分として含む分子量の大きい元素化合物からなる層や、結晶格子の小さい層によって、抑制層を構成しても良い。

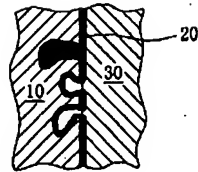
【0042】より広義には、本発明では、酸性物質を含む酸性酸化物と、酸性物質を含む複合酸化物と、窒素酸化物と上記吸蔵剤との反応性を阻害しない材料と、還元物質を吸着する材料とからなる群から選択される一つ以上の材料を含む材料から抑制層を形成可能であり、酸性物質は、ⅠⅤ族、Ⅴ族及びⅥ族の遷移元素ならびにⅠⅤ族、Ⅴ族及びⅥ族の典型元素から選択される一つ以上

10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 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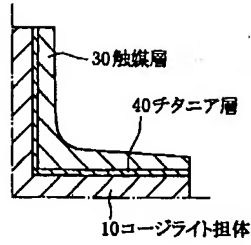
【図1】



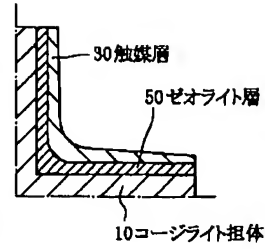
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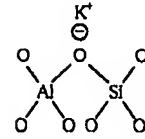
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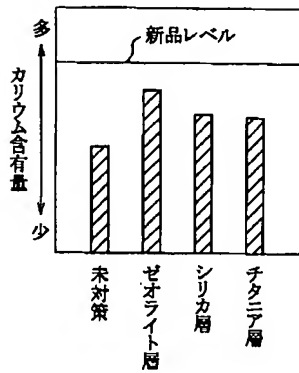
【図4】



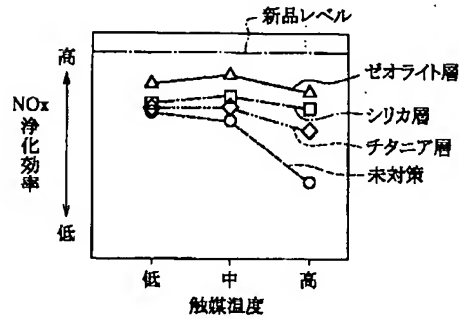
【図5】



【図6】



【図7】



フロントページの続き

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Fターム(参考) 4D048 AA06 AB01 BA03X BA03Y
BA06X BA06Y BA07X BA07Y
BA09X BA09Y BA11X BA11Y
BA14X BA14Y BA15X BA15Y
BA30X BB02 BB03 BC04
CC36 CC44 EA04
4G069 AA03 AA08 BA02B BA04B
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* NOTICES *

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3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]In a catalyst for emission gas purification which adds at least one chosen from a group which becomes this catalyst bed from an alkaline metal and alkaline-earth metals including a carrier and a catalyst bed as an occlusion agent, A catalyst for emission gas purification providing a restraining layer into a catalyst and controlling movement of the above-mentioned occlusion agent in the above-mentioned catalyst.

[Claim 2]A catalyst for emission gas purification given in the 1st paragraph of a claim forming the above-mentioned restraining layer in at least one place of between the above-mentioned carrier and the above-mentioned catalyst beds and the inside of the above-mentioned catalyst bed, or an outside surface of the above-mentioned catalyst bed.

[Claim 3]A catalyst for emission gas purification given in the 1st paragraph of a claim or the 2nd paragraph comprising one or more materials characterized by comprising the following chosen from a group.

An acidic oxide in which the above-mentioned restraining layer contains at least one acid chosen from a representative element of a transition element of group IV, V fellows, and a VI group and group IV, V fellows, and a VI group.

the above -- a multiple oxide which contains one acid even if small.

Material which does not check the reactivity of nitrogen oxides and the above-mentioned occlusion agent.

Material which adsorbs a reducing substance.

[Claim 4]A catalyst for emission gas purification given in the 1st paragraph of a claim or the 2nd paragraph, wherein the above-mentioned restraining layer consists of zeolite.

[Claim 5]A catalyst for emission gas purification given in either of the 1st paragraph of a claim thru/or the 4th paragraph to which the above-mentioned occlusion agent is characterized by

the above-mentioned carrier consisting of porous carriers including potassium.

[Claim 6]A catalyst for emission gas purification given in the 1st paragraph of a claim, the 2nd paragraph, or the 5th paragraph, wherein the above-mentioned restraining layer comprises any one of a layer with high acidity, a layer with high specific surface area, a layer with a small crystalline lattice, a layer that consists of element compounds with a large molecular weight, or the layers with a high basicity.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]Especially this invention relates to the catalyst for emission gas purification excellent in endurance and exhaust gas purification performance about the catalyst for emission gas purification.

[0002]

[A related background art] Lean combustion type engine, such as a lean burn engine and a cylinder injection type engine, is operated rather than theoretical air fuel ratio in a predetermined operation area by the lean air fuel ratio by the side of fuel thin for improvement in the fuel consumption characteristic or the exhaust gas characteristic. While lean air fuel ratio operation is performed, NOx (nitrogen oxides) in exhaust gas from the ability not to fully purify with a three way component catalyst. Reducing the NOx emission to the atmosphere is known by equipping the NOx catalyst which carries out occlusion of the NOx in exhaust gas in an oxidizing atmosphere, and making NOx by which occlusion was carried out to this catalyst return to N2 (nitrogen) by reducing atmosphere. In this kind of occlusion type lean NOx catalyst, there is a thing adds potassium (K) as a NOx occlusion agent, and the NOx occlusion performance was made to improve like the statement to JP,9-85093,A.

[0003]

[Problem(s) to be Solved by the Invention]However, the NOx catalyst which added the occlusion agent, for example, potassium, may be crossed to a long time, a crack may occur for a catalyst also under an elevated temperature, and it has become a cause of the durability degradation of a NOx catalyst. In order to investigate the cause of the crack generation in a NOx catalyst this invention persons, The NOx catalyst which adds potassium as an occlusion agent to the catalyst bed supported to the honeycomb type cordylite carrier was manufactured, and the driving test of the vehicles carrying the engine bench test of the engine which

equipped this NOx catalyst, and this kind of engine was done. In the engine bench test or the real vehicle driving test, an engine and vehicles were operated on conditions which are put to the elevated temperature more than 650 degreeC, over the time when a NOx catalyst is considerable. And ultimate analysis in the cutting plane of a NOx catalyst is carried out by the EPMA method (electron beam probe minute-sections analysis method) after the end of operation, It checked that compound KAlSiO_4 of compound $\text{KMg}_4\text{aluminum}_9\text{Si}_9\text{O}_{36}$ of potassium, magnesium, aluminum, silicon, and oxygen, potassium, aluminum, silicon, and oxygen existed in the cordylite ($\text{Mg}_2\text{aluminum}_4\text{Si}_5\text{O}_{18}$) layer of a catalyst.

[0004]According to the above-mentioned experiment, if a NOx catalyst is put to an elevated temperature, the potassium added by the catalyst bed (wash coat) will permeate in a cordylite carrier, and it will be thought that potassium reacts to a cordylite and the above-mentioned compound is formed under a high temperature atmosphere. Here, since the water solubility is high and the melting point is low, the compound of potassium is understood that potassium permeates a cordylite carrier easily. And when a cordylite and the compound which differs in a coefficient of thermal expansion are formed into a cordylite carrier, a crack will occur in a cordylite carrier with change of the catalyst temperature under catalyst use and before and behind use, and the intensity of a NOx catalyst will fall.

[0005]As mentioned above, the NOx catalyst which contains potassium etc. as an occlusion agent is used under an oxidizing atmosphere. In this oxidizing atmosphere, the nitrate and sulfate of an occlusion agent are formed of the chemical reaction of an occlusion agent, and the nitrogen component in exhaust gas and a sulfur component, and NOx occlusion capacity declines. In this case, although occlusion capacity is recoverable by forming reducing atmosphere and decomposing a nitrate and sulfate into the circumference of a NOx catalyst, even if it takes such a measure, when a NOx catalyst is used under an elevated temperature for a long time, purification performance may fall.

[0006]In view of the result of the following experiment which this invention person conducted, it is thought that one of the purification performance fall causes is in an occlusion agent evaporating and dispersing gradually from a NOx catalyst in the bottom of an elevated temperature, and most portion of the occlusion agent within a catalyst disappearing. Namely, this invention person manufactures the NOx catalyst which supports the catalyst bed which contains potassium as an occlusion agent to a cordylite carrier, It asks for the potassium content in an intact NOx catalyst by the XRF method (X ray fluorescence spectroscopy), Next, after using this catalyst over a long time (it is 32 hours for example, at 850 degreeC) under an elevated temperature, it asked for the potassium content of the catalyst, and further, the difference of the potassium content before and behind use was ^{**}(ed) with the original potassium content, and the amount of potassium disappearance was calculated. As a result, it turned out that the amount of potassium disappearance reaches to tens of % thru/or 50% (see

drawing 6).

[0007]Then, an object of this invention is to provide the catalyst for emission gas purification which can be reduced substantially for the aggravation degree of the exhaust gas purification performance by disappearance of an occlusion agent.

[0008]

[Means for Solving the Problem]This invention provides a restraining layer which becomes a catalyst for emission gas purification which adds an occlusion agent to a catalyst bed from material which controls movement of an occlusion agent, and controls movement of an occlusion agent in a catalyst. As for an occlusion agent which moves in inside of a catalyst when a catalyst for emission gas purification is exposed to an elevated temperature, movement is controlled by restraining layer in this invention. A restraining layer makes the shape of a layer, a formation gestalt of such a restraining layer contributes to control of movement of an occlusion agent greatly, and, as for evaporation of an occlusion agent from a catalyst, and disappearance ***** of an occlusion agent by scattering, a fall of exhaust gas purification performance of a catalyst is prevented.

[0009]In this invention, a restraining layer is preferably constituted by material which has an acid site. In this case, an occlusion agent which moves in inside of a catalyst is understood as what is caught and fixed in an acid site which a component of a restraining layer has, and can control movement of an occlusion agent in a catalyst effectively. In this invention, a restraining layer is preferably formed between a carrier and catalyst beds or in either [at least] an outside surface of a catalyst bed.

[0010]When it provides between a carrier and a catalyst bed, for example a carrier is covered with a restraining layer, permeation into a carrier of an occlusion agent added by catalyst bed is certainly prevented by restraining layer which made the shape of a layer and was provided between a catalyst bed and a carrier. And since permeation of an occlusion agent into a carrier is controlled by restraining layer, formation of a compound by a reaction of a composition component of material and a composition component of a carrier which constitute an occlusion agent is controlled, and durability degradation of ** from a crack in a carrier resulting from formation of this compound and by extension, a catalyst is prevented. When a restraining layer is formed in an outside surface of a catalyst bed, evaporation of an occlusion agent from a catalyst bed and scattering are certainly prevented by restraining layer which made and provided the shape of a layer in an outside surface of a catalyst bed. A thing provided with two or more catalyst beds may be sufficient as a catalyst of this invention, and one or two restraining layers or more are allotted to a proper position in a catalyst in this case according to arrangement of a catalyst bed.

[0011]In a catalyst which generally supports a catalyst bed to a carrier which consists of many cells. In order to satisfy mechanical, physical, or chemical requirements imposed on catalysts,

such as prevention from exfoliation of a catalyst bed from a carrier surface, in a corner part of each cell of a carrier, thickness of a catalyst bed is thickened, therefore a catalyst bed will have a depths part near a corner part. Make an exhaust air fuel ratio rich, and form reducing atmosphere in order to decompose sulfate generated by reaction of an occlusion agent in a catalyst bed, and a sulfur component in fuel and to recover occlusion performance, as already stated, but. In a depths part of a catalyst bed, since gas diffusion is bad, decomposition of sulfate is difficult, particle growth of sulfate advances easily, and NO_x occlusion performance falls by consumption of an occlusion agent accompanying this.

[0012]In a suitable mode of this invention which forms a restraining layer between this point, a carrier, and catalyst beds and in an outside surface of a catalyst bed. Requirements that a catalyst bed of a carrier corner part should be made thick are eased, thickness of a catalyst bed is made uniformly as a whole, gas diffusion in a catalyst bed is promoted, and an amount of consumption of an occlusion agent accompanying growth of sulfate decreases. In this invention, a restraining layer comprises preferably at least one material chosen from a group which consists of a multiple oxide containing acid. Each of a multiple oxide containing acid contains at least one acid chosen from a group which consists of a representative element of a transition element of group IV, V fellows, and a VI group and group IV, V fellows, and a VI group.

[0013]In this suitable mode, prevention and durability enhancement of an exhaust gas purification performance fall of a catalyst are planned with an acidic oxide and a multiple oxide which are rich in occlusion agent fixed capability and thermal stability. For example, a multiple oxide comprises an oxide of combination which an acid site reveals. At least one acid is more preferably chosen in consideration of the reactivity of acid and an occlusion agent. For example, when an occlusion agent is potassium, it is good to use an acidic oxide which contains silica and tungsten as acid, and a multiple oxide.

[0014]Preferably, a restraining layer consists of material which does not check the reactivity of NO_x and an occlusion agent. In this case, an operation which controls movement of an occlusion agent on a catalyst is done so by restraining layer, and a NO_x occlusion operation of an occlusion agent is done so good. Or a restraining layer consists of material which adsorbs a reducing substance (for example, reducing gas, such as HC). In this case, sulfate and a nitrate in a catalyst bed and a restraining layer are decomposed by reducing substance caught by reducing substance adsorption capacity of a restraining layer in a restraining layer, and NO_x occlusion performance is recovered.

[0015]Preferably, a restraining layer consists of zeolite. According to the catalyst provided with zeolite as a restraining layer, an advantage of an already described suitable mode and same advantage are done so. That is, zeolite has cation exchange ability and a molecular sieve operation, and is excellent in capability to adsorb capability and HC which fix an occlusion

agent. It may have been ionized under a hot steam existence by occlusion agent which moves in inside of a catalyst, and it is fixed by cation exchange ability of an acid site on zeolite as ion (see drawing 5). Zeolite has three-dimensional network structure and has high specific surface area. Since an occlusion agent is high-decentralized on zeolite of such a structure, when especially zeolite is provided between a catalyst bed and a carrier, an occlusion agent becomes difficult to permeate into a carrier. Zeolite is excellent in HC adsorption capacity (generally reducing substance adsorption capacity). Even if an internal-combustion engine is in a lean operation state, slight HC is contained in exhaust gas, and decomposition of a nitrate of an occlusion agent or sulfate is promoted by HC which adsorbed on zeolite. That is, a restraining layer which consists of zeolite which has HC adsorption capacity during lean operation decomposes a nitrate and sulfate of an occlusion agent continuously using slight HC contained in exhaust gas, and contributes to recovery of NO_x occlusion performance of a catalyst.

[0016]In this invention, although it is usable as zeolite which constitutes a restraining layer in zeolite of various types, such as a MFI type, Y type, an X type, mordenite, and a ferrierite, it is preferred to choose what suits an exhaust gas presentation in consideration of structure relevance with an adsorption HC kind. It depends for cation exchange ability and heat-resistant performance of zeolite on a composition component of zeolite. That is, in inverse proportion to SiO₂/AlO₂ ratio in zeolite, heat resistance of cation exchange ability is proportional to this ratio. Therefore, for example, improvement in heat-resistant of a catalyst can be aimed at by enlarging the above-mentioned ratio as much as possible. By making the above-mentioned ratio small, the amount of disappearance of an occlusion agent accompanying prolonged operation under an elevated temperature of a catalyst is reduced, and occlusion performance can be maintained.

[0017]Preferably, a restraining layer does not contain a catalyst substance, for example, the precious metals. In this case, within a restraining layer, a catalysis by a catalyst substance is not done so, but since it becomes difficult to produce a chemical reaction of an occlusion agent fixed to a restraining layer, and SO_x in exhaust gas, consumption of an occlusion agent accompanying this chemical reaction decreases, and NO_x occlusion performance of a catalyst is maintained. In this invention, as for an occlusion agent, a carrier consists of porous carriers preferably including potassium. NO_x occlusion capacity of a catalyst improves by addition of potassium. Pressure loss of exhaust gas declines by use of a porous carrier, and exhaust gas contacts a catalyst bed good and emission gas purification is performed good. Although circulation of exhaust gas containing a hot steam becomes good and it becomes easy to produce movement of an occlusion agent, evaporation, and scattering on the other hand with a catalyst which has a porous carrier, this is prevented by restraining layer in this invention.

[0018]The above-mentioned restraining layer comprises any one of a desirable layer with high

acidity, a layer with high specific surface area, a layer with a small crystalline lattice, a layer that consists of element compounds with a large molecular weight, or the layers with a high basicity. Preferably, a layer with high acidity contains, an acid material with high reactivity, for example, a silicon oxide, with potassium of a catalyst bed. A layer with high specific surface area contains, high material, for example, zeolite, of specific surface area. A layer which consists of element compounds with a large molecular weight comprises, for example, base material (BaSO_4), for example, barium sulfate, with it. [a large and molecular weight and] [stable] A layer with a high basicity consists of base materials, such as barium oxide (BaO), for example.

[0019]According to the above-mentioned suitable mode, osmosis of potassium to a porous carrier is considered to be controlled by the following mechanism. That is, when a restraining layer comprises a layer with high acidity, potassium is understood as what is consumed before reacting to a layer with high acidity and reaching on the surface of a porous carrier. Inside a restraining layer which consists of a layer with high specific surface area, potassium high-distributes and a restraining layer which consists of a layer with a small crystalline lattice is understood to prevent movement of potassium. In the case of a restraining layer which consists of element compounds with a large molecular weight, it is thought that an osmosis course of potassium to a porous carrier decreases. And since this layer has the same character as potassium in the case of a restraining layer with a high basicity, if potassium approaches a restraining layer, rebounding will be received, and it is understood as that to which the inductivity of potassium to a porous carrier falls.

[0020]Osmosis of potassium to a porous carrier is controlled as mentioned above, and durability enhancement of an exhaust gas cleaning catalyst is planned. In the case of a restraining layer which can control the osmosis, without consuming potassium, a fall of a NO_x cleaning effect of potassium by consumption of potassium is not caused, and exhaust gas purification performance of a catalyst for emission gas purification is maintained suitably. In order to evaluate the endurance of a catalyst for emission gas purification of this invention, and occlusion agent disappearance prevention capability, A NO_x catalyst which provides zeolite as a restraining layer between a catalyst bed and a cordylite carrier which added an occlusion agent which contains potassium as the example was manufactured, and it asked for potassium content in an intact NO_x catalyst by the XRF method. Carry a NO_x catalyst in an engine and an engine bench test and a real vehicle driving test are presented, It asked for potassium content of a NO_x catalyst which this used over a long time (it is 32 hours for example, at 850 degreeC) under an elevated temperature, and asked for what ^{**}(ed) a difference of potassium content before and behind use with the original potassium content as an amount of potassium disappearance. As a result, with a catalyst which supported a catalyst bed to a carrier, it turned out that the amount of potassium disappearance which reaches to tens of % thru/or 50% is

controlled to about about ten% with a catalyst of this invention. This experimental result (drawing 6) shows that the amount of disappearance from a catalyst of potassium which is an occlusion agent is substantially reduced by this invention.

[0021]After presenting an engine bench test and a real vehicle driving test with the above-mentioned NOx catalyst by this invention, ultimate analysis was conducted by the EPMA method about the cutting plane. As a result, it was admitted that the surface of a cordylite carrier had fairly little abundance of a compound of a compound of potassium within a cordylite carrier, magnesium, aluminum, silicon, and oxygen, potassium, aluminum, silicon, and oxygen compared with a case of a catalyst which only forms a catalyst bed.

[0022]This experimental result shows that osmosis of potassium to inside of a cordylite carrier (generally porous carrier) is prevented by restraining layer. Generation of a compound resulting from osmosis of potassium is prevented, it is hard to generate a crack in a porous carrier, and a catalyst for emission gas purification of this invention is actually rich in endurance, also when it is used under an elevated temperature for a long time.

[0023]

[Embodiment of the Invention]Hereafter, the exhaust gas purifying catalyst by a 1st embodiment of this invention is explained. The exhaust gas purifying catalyst of this embodiment is constituted as a NOx catalyst which has a honeycomb (monolith) type cordylite carrier which consists of many cells. Drawing 1 shows a part of one cell of a cordylite carrier, and the cell of the cordylite carrier 10 is formed in quadrangular shape. The silica layer 20 is covered by the surface of the cordylite carrier 10, and the catalyst bed 30 is supported by the surface of the silica layer 20. And potassium (K) and barium (Ba) are added by the catalyst bed 30 as a NOx occlusion agent. The silica layer 20 functions as a restraining layer which controls osmosis of the potassium to the cordylite carrier 10 (generally porous carrier).

[0024]The cordylite carrier 10, for example the powder of an alumina source, the powder of a silica source, and the powder of the source of magnesia, Water is made to distribute what was mixed so that the rate of alumina, silica, and magnesia might become a cordylite presentation, that solid content is fabricated to honeycomb shape, and this honeycomb Plastic solid is calcinated. The silica layer 20 is formed in the surface of the cordylite carrier 10 as follows, for example. First, the water soluble salt of a silicon compound is diluted with water, the solution of prescribed concentration is prepared, and the cordylite carrier 10 is immersed into this solution. The solution of the salt of a silicon compound is absorbed by the absorptivity of the cordylite carrier 10 in the surface of the cordylite carrier 10, or a surface. Then, the cordylite carrier 10 is dried, moisture is evaporated and the salt of a silicon compound is made to adsorb into the surface of the cordylite carrier 10, or a surface. Next, if the cordylite carrier 10 is heated, the salt of a silicon compound will decompose and the silica layer 20 will be formed in the surface of the cordylite carrier 10. That is, the cordylite carrier 10 is covered with the

silica layer 20.

[0025]The proper concentration of the solution of the salt of the silicon compound used for formation of the silica layer 20 changes mainly according to the water absorption characteristic of the cordylite carrier 10. Then, it is preferred to conduct ultimate analysis by the EPMA method etc. about the layer part of a cordylite carrier, and to check beforehand the relation between aqueous solution concentration and a coated state. Thus, by asking for the optimum density of the solution of the salt of a silicon compound beforehand, the optimal coated state that collateralizes the adhesive property of a cordylite carrier and a catalyst bed and the potassium percolation control effect of a silica layer can be acquired.

[0026]The catalyst bed 30 is formed in the surface of the silica layer 20 as follows, for example. First, the slurry containing the powder which uses the precious metals, such as PURACHINA, alkaline metals, such as potassium, and alkaline-earth metals, such as barium, as the main ingredients is prepared. Subsequently, the cordylite carrier 10 whose silica layer 20 has been formed is immersed into the above-mentioned slurry, and after drying this, it calcinates.

[0027]The NO_x catalyst which coats the cordylite carrier 10 with the catalyst bed 30 via the silica layer 20 as mentioned above is acquired. Conventionally, this NO_x catalyst is accommodated in a case, for example via shock absorbing material, and is arranged in the exhaust pipe of an internal lean combustion engine so that it may be publicly known. According to this NO_x catalyst, occlusion of the NO_x in exhaust gas is carried out in the form of a nitrate under an operation of the catalyst species distributed by the catalyst bed 30 during the engine operation in a lean air fuel ratio. A nitrate is disassembled during the engine operation in a rich air fuel ratio, it is returned to nitrogen and NO_x by which occlusion was carried out is emitted into the atmosphere from a NO_x catalyst.

[0028]If the internal-combustion engine which equipped such a NO_x catalyst is operated for a long time, a NO_x catalyst will be exposed to an elevated temperature over a long time. In this case, if it is in the conventional NO_x catalyst which coats a cordylite carrier with the catalyst bed by which potassium was added, As already stated, potassium will move into a cordylite carrier, it will react to silicon in a carrier, etc., and a compound will be generated, a crack will occur in a cordylite carrier, and the endurance of a NO_x catalyst will be spoiled. On the other hand, in the NO_x catalyst of this embodiment, according to the ultimate analysis by the EPMA method, also when a NO_x catalyst was used under an elevated temperature over a long time, it became clear that generation of the compound of the potassium added by the catalyst bed 30 and the silica components of the cordylite carrier 10 is controlled. This reason is considered that movement of the potassium from the catalyst bed 30 to the cordylite carrier 10 is prevented by the silica layer 20. Thus, since the compound which differs in the cordylite carrier 10 and a coefficient of thermal expansion does not generate in the cordylite carrier 10, the

crack generation in the cordylite carrier 10 resulting from generation of a compound is prevented.

[0029]Hereafter, the exhaust gas purifying catalyst by a 2nd embodiment of this invention is explained. As shown in drawing 3, the exhaust gas purifying catalyst of this embodiment is replaced with the silica layer 20 compared with the thing of a 1st embodiment, and the points which formed the titania layer 40 which uses a titanium dioxide (TiO_2) as the main ingredients as a restraining layer differ. About other points, it is the thing and identical configuration of a 1st embodiment, and this exhaust gas purifying catalyst can be manufactured by the method of the approximately said appearance as the thing of a 1st embodiment.

[0030]Also in the exhaust gas purifying catalyst of this embodiment which forms the titania layer 40 between the cordylite carrier 10 and the catalyst bed 30, According to the ultimate analysis by the EPMA method, also when [under the elevated temperature covering a long time] it was used, it turned out that osmosis into the cordylite carrier 10 of the potassium added by the catalyst bed 30 is prevented. Thus, since osmosis of potassium is prevented, this exhaust gas cleaning catalyst is rich in endurance. In the NO_x catalyst by this embodiment, the loss of the potassium from the catalyst bed 30 is reduced. It is thought that this reason is the same as that of a silica layer.

[0031]Hereafter, the exhaust gas purifying catalyst by a 3rd embodiment of this invention is explained. As shown in drawing 4, the exhaust gas purifying catalyst of this embodiment is replaced with the silica layer 20 compared with the thing of a 1st embodiment, and the points which formed the zeolite layer 50 as a restraining layer differ. About other points, it is the thing and identical configuration of a 1st embodiment, and this exhaust gas purifying catalyst can be manufactured by the method of the approximately said appearance as the thing of a 1st embodiment.

[0032]Although a drainage system dispersing agent may be made to distribute a zeolite constituent like the case of a 1st embodiment in formation of the zeolite layer 50 to the cordylite carrier 10, it may be made to distribute an organic nature dispersing agent. The underwater distribution article (sol) and electrification dispersed solutions (colloid) of a hydrate, such as silica and alumina, can also be used as adhesives.

[0033]In the catalyst of this embodiment provided with the zeolite layer 50 as a restraining layer, the zeolite layer 50 has an acid site provided with cation exchange ability, and is excellent in the capability to fix an occlusion agent (this embodiment potassium). As it may have been ionized under a hot steam existence by the occlusion agent which moves in the inside of a catalyst and it is typically shown in drawing 5, an occlusion agent, for example, potassium, is fixed by the cation exchange ability of the acid site on the zeolite layer 50 as ion. The zeolite layer 50 has three-dimensional network structure, and has high specific surface area. Since it high-distributes on the zeolite of such a structure, potassium becomes difficult to

permeate into the cordylite carrier 10. The zeolite layer 50 is excellent in the capability to adsorb a reducing substance (for example, reducing gas, such as HC). Even if an internal-combustion engine is in a lean operation state, slight HC is contained in exhaust gas, and decomposition of the nitrate of potassium or sulfate is promoted by HC which adsorbed on the zeolite layer 50 which has HC adsorption capacity. That is, during lean operation, the zeolite layer 50 decomposes a nitrate and sulfate continuously using slight HC contained in exhaust gas, and contributes to recovery of the NO_x occlusion performance of a catalyst.

[0034]The zeolite layer 50 of this embodiment does not contain the precious metals, such as a catalyst substance, for example, Pt etc., Therefore, within the zeolite layer 50, the catalysis by Pt etc. is not done so, but since it becomes difficult to produce the chemical reaction of SO_x in the potassium fixed to the zeolite layer 50, and exhaust gas, consumption of the occlusion agent accompanying such a chemical reaction decreases, and the NO_x occlusion performance of a catalyst is maintained.

[0035]The zeolite layer 50 can be constituted using the zeolite of various types, such as a MFI type, Y type, an X type, mordenite, and a ferrierite. Under the present circumstances, in consideration of structure relevance with an adsorption HC kind, the zeolite of the type which suits an exhaust gas presentation is chosen. In inverse proportion to the SiO₂/AlO₂ ratio in zeolite, that heat resistance of the cation exchange ability of zeolite is proportional to this ratio. The above-mentioned ratio is made to become as large as possible in this embodiment for the improvement in heat-resistant. By preparing a zeolite composition component so that SiO₂/AlO₂ ratio may become small, it can increase and the amount of disappearance of the occlusion agent by the prolonged use under an elevated temperature reduces the occlusion agent capturing capacity power of zeolite in this case.

[0036]In order to evaluate the endurance of the exhaust gas purifying catalyst of this embodiment and occlusion agent disappearance prevention capability to form the zeolite layer 50 between the cordylite carrier 10 and the catalyst bed 30, The NO_x catalyst which provides zeolite as a restraining layer between the catalyst bed and cordylite carrier which added the occlusion agent containing potassium was manufactured, and it asked for the potassium content in an intact NO_x catalyst by the XRF method. Carry a NO_x catalyst in an engine and an engine bench test and a real vehicle driving test are presented, It asked for the potassium content of the NO_x catalyst which this used over the long time (it is 32 hours for example, at 850 degreeC) under the elevated temperature, and asked for what ^{**}(ed) the difference of the potassium content before and behind use with the original potassium content as an amount of potassium disappearance.

[0037]It is shown in drawing 6 with the experimental result about the catalyst of a 2nd embodiment that formed the catalyst which is not coped with [which supported the catalyst bed for the experimental result about the catalyst of this embodiment which formed the zeolite

layer 50 to the carrier], the catalyst of a 1st embodiment that formed the silica layer 20, and the titania layer 40. As shown in drawing 6, with the catalyst of this embodiment, it turned out to the amount of potassium disappearance in an uncoped with catalyst reaching to tens of % thru/or 50% that this amount of potassium disappearance is controlled to about about ten%. This experimental result shows that the amount of disappearance from the catalyst of the potassium which is an occlusion agent is reduced substantially. The amount of potassium disappearance in the catalyst of 1st and 2nd embodiments was about about twenty%.

[0038]Like the case of the 1st and 2nd examples, after presenting an engine bench test and a real vehicle driving test with the catalyst of this embodiment, ultimate analysis was conducted by the EPMA method about the cutting plane. As a result, also when [under the elevated temperature covering a long time] it was used, it turned out that osmosis into the cordylite carrier 10 of the potassium added by the catalyst bed 30 is prevented. this invention is not limited to the thing of the above-mentioned embodiment, but is deformable to versatility.

[0039]For example, in the above-mentioned embodiment, although the honeycomb type cordylite carrier 10 was used as a carrier, this invention is applicable also to the catalyst for emission gas purification provided with the carrier which comprises materials other than a cordylite. When a metal carrier is used, although osmosis of the occlusion agent to a carrier hardly becomes a problem, the effect of preventing scattering of an occlusion agent is acquired and the fall of the exhaust gas purification performance of a catalyst is prevented. When using a honeycomb type cordylite carrier, the cell of a cordylite carrier may not be limited to the thing of quadrangular shape, for example, the thing of triangular shape or the shape of a hexagon may be sufficient as it.

[0040]Although the silica layer 20 which uses a silicon dioxide as the main ingredients in a 1st embodiment constituted the restraining layer, and the titania layer 40 which uses a titanium dioxide as the main ingredients constituted the restraining layer from a 2nd embodiment and the zeolite layer 50 constituted the restraining layer from a 3rd embodiment, The component of a restraining layer is limited to neither a silicon dioxide nor a titanium dioxide nor zeolite.

[0041]That is, it can replace with a silicon dioxide and a layer with high acidity can constitute a restraining layer using other acid materials. It can replace with a titanium dioxide and a layer with a high basicity which uses base materials, such as alkaline metals, such as barium (Ba), and barium oxide (BaO), as the main ingredients can constitute a restraining layer. A layer with high specific surface area which includes material with high specific surface area of zeolite etc. as the main ingredients, the layer which consists of element compounds with a large molecular weight which contains as the main ingredients, stable base material, for example, barium sulfate, with a large molecular weight, and a layer with a small crystalline lattice may constitute a restraining layer.

[0042]The acidic oxide which contains the acid in a broad sense by this invention more, and

the multiple oxide containing the acid, A restraining layer can be formed from the material containing one or more materials chosen from the group which consists of material which does not check the reactivity of nitrogen oxides and the above-mentioned occlusion agent, and material which adsorbs a reducing substance, The acid may include one or more materials chosen from the representative element of the transition element of group IV, V fellows, and a VI group and group IV, V fellows, and a VI group.

[0043]In the above-mentioned embodiment, although the one restraining layer 20, 40, or 50 was formed in the outside surface of the carrier 10 between the carrier 10 and the catalyst bed 30, the number of formation and formation part of a restraining layer are not limited to this. For example, one restraining layer can be formed in the outside surface of the catalyst bed 30. In the case of the catalyst which has two or more catalyst beds, according to the formation mode of a catalyst bed, one or two restraining layers or more can be suitably formed in at least one place of between a carrier and catalyst beds and the inside of a catalyst bed, or the outside surface of a catalyst bed.

[0044]

[Effect of the Invention]Since the catalyst for emission gas purification concerning the invention according to claim 1 provides a restraining layer into a catalyst and controlled movement of the occlusion agent in a catalyst, evaporation of an occlusion agent and the disappearance ***** of the occlusion agent by scattering can reduce the fall of the exhaust gas purification performance of a catalyst substantially. In the invention according to claim 2, since the restraining layer was formed in at least one place of between a carrier and catalyst beds and the inside of a catalyst bed, or the outside surface of a catalyst bed, Permeation into the carrier of the occlusion agent added by the catalyst bed, evaporation of the occlusion agent from a catalyst bed, and scattering can be certainly prevented by the restraining layer which makes the shape of a layer, and prevention from a fall of the durability enhancement of a catalyst or exhaust gas purification performance can be aimed at.

[0045]The acidic oxide or multiple oxide which contains at least one acid chosen from the transition element and representative element of group IV, V fellows, and a VI group in the invention according to claim 3, Since a restraining layer is constituted from one or more materials chosen from the group which consists of material which does not check the reactivity of nitrogen oxides and an occlusion agent, and material which adsorbs a reducing substance, Controlling disappearance of an occlusion agent with the material which can plan prevention and durability enhancement of an exhaust gas purification performance fall of a catalyst with the acidic oxide and multiple oxide which are rich in occlusion agent fixed capability and thermal stability, and does not check the reactivity of nitrogen oxides and an occlusion agent. Emission gas purification by NOx occlusion operation of an occlusion agent can be attained, an occlusion agent is reproduced using the reducing substance which the material which has

reducing substance adsorption capacity caught, and exhaust gas cleaning capacity can be recovered.

[0046]In the invention according to claim 4, since the restraining layer was constituted from zeolite, movement of the occlusion agent in a catalyst is effectively prevented by the cation exchange ability of zeolite, and evaporation of an occlusion agent and the disappearance ***** of the occlusion agent by scattering can prevent an exhaust gas purification performance fall.

In the invention according to claim 5, the osmosis in the carrier of an occlusion agent, evaporation, and scattering which are easy to produce when a porous carrier is used can be effectively prevented by a restraining layer, aiming at improvement in occlusion capacity by potassium, and improvement in the exhaust gas purification performance by a porous carrier.

[0047]In the invention according to claim 6, since the restraining layer was constituted from any one of a layer with high acidity, a layer with high specific surface area, a layer with a small crystalline lattice, the layer that consists of element compounds with a large molecular weight, or the layers with a high basicity, movement of an occlusion agent can be prevented certainly. When a restraining layer is especially constituted from a layer with a high basicity, etc., movement of an occlusion agent can be prevented without causing the loss of the occlusion agent from a catalyst bed, and the cleaning effect of an occlusion agent can be maintained.

[Translation done.]

* NOTICES *

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a partial expanded sectional view showing four half parts of one shell of the catalyst for emission gas purification by a 1st embodiment of this invention.

[Drawing 2] It is a mimetic diagram for explaining the formed state of the silica layer in the inside of the fine pores of a cordylite carrier.

[Drawing 3] It is a partial expanded sectional view showing four half parts of one shell of the catalyst for emission gas purification by a 2nd embodiment of this invention.

[Drawing 4] It is a partial expanded sectional view showing four half parts of one shell of the catalyst for emission gas purification by a 3rd embodiment of this invention.

[Drawing 5] It is a mimetic diagram showing the potassium fixation operation by the cation exchange ability of the zeolite which constitutes the restraining layer of the catalyst shown in drawing 4.

[Drawing 6] It is a figure shown with the thing of the catalyst which showed an uncoped with catalyst, the catalyst shown in drawing 1, and drawing 3 the kalium content after using the catalyst shown in drawing 4 under an elevated temperature for a long time.

[Drawing 7] It is a figure shown with the thing of the catalyst which showed an uncoped with catalyst, the catalyst shown in drawing 1, and drawing 3 the NOx purification efficiency after using the catalyst shown in drawing 4 under an elevated temperature for a long time.

[Description of Notations]

- 10 Cordylite carrier
- 20 Silica layer
- 30 Catalyst bed
- 40 Titania layer
- 50 Zeolite layer

[Translation done.]

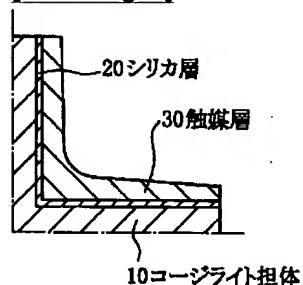
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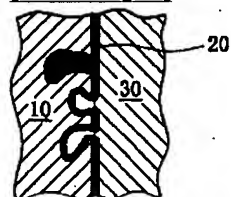
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DRAWINGS

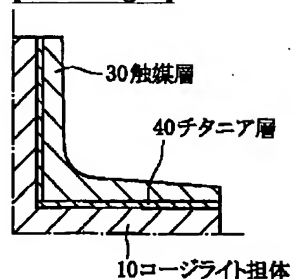
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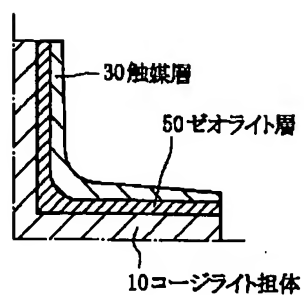
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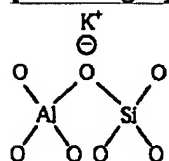
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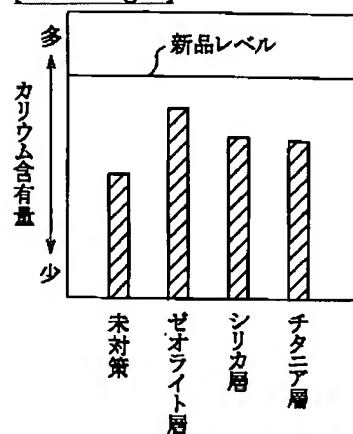
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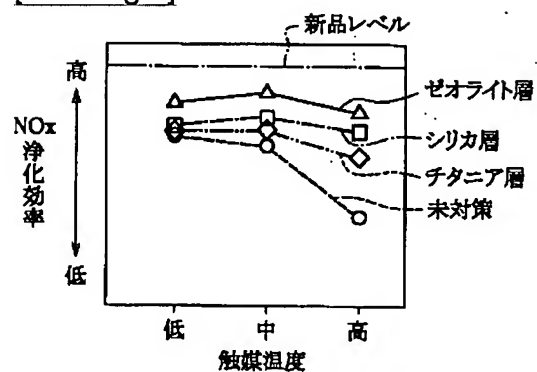
[Drawing 5]



[Drawing 6]



[Drawing 7]



[Translation done.]